

Chemistry of the Sea

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We might well begin a consideration of the chemistry of the sea by recalling the words in Ecclesiastes. "All the rivers run into the sea, yet the sea does not overflow; unto the place from whence the rivers came, they return to flow again" (Eccl. 1:7). The writer of these words, if not familiar with the sea, was at least intuitively aware of the existence of a cyclic process that we recognize as being so very typical of the chemistry of the sea. His words suggest a basic question that we still are trying to answer and at this time we can give only a partial answer: What is the nature of the sea water, how did it come to be, and what are the consequences of the processes that brought it to its present state?

The nature of sea water is one of evident constancy, as indicated by three observations. First, a number of the major constituents of sea water (Table 1), i.e., those present in concentrations of 1 ppm or greater, show an evident constancy of composition. By this we mean that the weight ratio of, say, magnesium (or sodium or potassium) to chloride is constant for a given type of sea water. Second, the pH of sea water tends to be remarkably constant (8.1 ± 0.2)

TABLE 1
Major constituents of sea water

Constituent	Amount g/kg sea water
Water	
Chloride	19.353
Sodium	10.76
Sulfate	2.712
Magnesium	1.294
Calcium	0.413
Potassium	0.387
Bicarbonate	0.142
Bromide	0.067
Strontium	0.0080
Boron	0.0045
Fluoride	0.001

Average salinity, 35 parts per thousand (35 g of dissolved salts per kg of sea water).

at the mean temperature of sea water (5 C). Finally, many believe that the composition and pH of sea water has not altered significantly during the past 100 million years (Sillén, 1967a).

The geochemical balance is one approach that has been used to arrive at the rationalization of the present nature of the sea. This may be represented by a process first suggested by Goldschmidt nearly 40 years ago (Equation 1) (Sillén, 1967a).

(1) Igneous rock + Volatiles \rightleftharpoons Sea Water + Sediment + Atmosphere.

Goldschmidt assumed the process was unidirectional and that 0.6 kg of igneous rock reacted to produce each liter of sea water, together with 0.6 kg of sediment and 3 liters of atmosphere.

We would now modify Goldschmidt's approach in two ways. First, Horn and Adams (1966) were able to bring more elements (about 60) into geochemical balance by assuming that 1.2 kg of igneous rock and sediment were involved. Secondly, we would probably recognize that the reverse process occurs as an important feature of the cycle involved in sea-floor spreading. Neither of these changes would modify the conclusions arrived at by Goldschmidt's approach or Sillén's use of it to demonstrate the remarkable similarity between an equilibrium model of sea water and the properties of real sea water (Sillén, 1961).

Another difficulty arises. The geochemical balance may give us a good over-all view, but the subtleties or major physical-chemical processes are not immediately obvious.

The chemical and physical processes that control the present composition of sea water probably can be placed into several categories, for the sake of convenience. These include control by weathering, action of clays, crustal concentration, control by physical-chemical processes, and by organisms. The scope of this paper does not permit a thorough exploration of each of these, but examples can be given and reference made to more thorough treatments.

WEATHERING

The constancy of composition of sea water is astounding when we consider the effect of weathering, because the amounts of ions carried to the sea during the past 100 million years are enormous.

Weathering is the continued chemical interaction of rain with rocks and soil and is part of the cycle of interaction of sea and the earth's crust. The cycle consists of the evaporation of water from the sea, condensation as rain and snow, weathering, and chemical denudation of ions and suspended material via streams and rivers.

The extent of chemical denudation is uncertain because of the paucity of data for rivers of certain continents, notably Africa and Asia. The estimates of MacKenzie and Garrels (1966) have been used to calculate the amounts of ions added during the past 100 million years and to compare these with the present composition of sea water. (The units are moles of ion per square centimeter of earth surface, Table 2).

TABLE 2

Amount of dissolved ions added by rivers during 100 million years in comparison to present concentrations. (Sillen, 1967b)

	Cl ⁻	Na ⁺	SO ₄ ²⁻	Mg ²⁺	Ca ²⁺	K ⁺	CO ₃ ²⁻	NO ₃ ⁻
Added	157	196	84	122	268	42	342	11
Present								
Concentration*	150	129	8	13	2.8	2.7	0.3	0.01

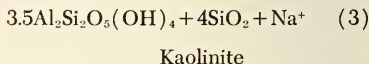
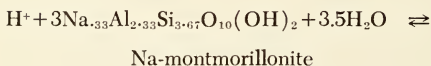
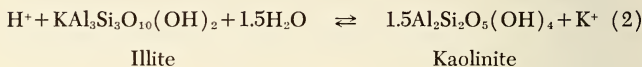
*Concentrations are expressed in units of moles per cm² of total earth surface

Three features deserve comment. First, it is evident that the amounts of ions added generally are much greater than those now present. (Exceptions are sodium and chloride ions; probably, these ions represent sea spray washed back.) Second, the amounts of elements added during 100 million years is much greater than would be evident because of the contribution by suspended solids (250-640 kg per cm² per 100 million years). Third, the amount of non-volatile dissolved solids in the sea is slight relative to the amount of sediment. Sillén (1967b) has provided an apt comparison: the dissolved solids (as oxides) would cover the earth with a uniform layer 20 m thick, but the sediments layer would be thousands of meters thick, and the radius of the earth is about 6,400,000 m.

The last feature, the large amount of sediment and suspended solids, is very significant because these materials have a clay-mineral content. The control of composition by these minerals deserves more attention than it has received.

ACTION OF CLAY MINERALS

Clay minerals are important in the marine environment because of their ion-exchange capacity. This capacity may be represented by two typical processes (equations 2-3). Many believe that these equations are responsible for three significant roles of clay minerals: control of the *pH* of sea water, maintenance of the concentration of certain ions (sodium, magnesium, potassium), and control of the silica concentration (at least for certain concentrations).



The significant features of the *pH* of sea water are (1) the apparent constancy (though changes occur in isolated bodies of water or because of biological activity), (2) the limited buffer capacity of an isolated 1-liter sample of sea water (0.003 mole of hydrochloric acid will reduce the *pH* from 8 to less than 4), (3) the buffer capacity of a liter of sea water in the ocean is great, perhaps 2000 times that for the isolated liter.

Sillén (1961) suggested that the major *pH* control mechanism in sea water is ion-exchange reactions (Equation 2) of clay minerals and that the carbonate system is mainly an indicator system. This is contrary to the view of many, but many arguments support Sillén's view (Martin, 1970). It appears that the time scale is an significant consideration. Pytkowicz (1967) believes that clay minerals have a significant effect in a geological time (ca. 1000 years) and that carbonate equilibria control *pH* in a shorter period of time.

Control of silica concentration by clay minerals (Eqn 3) appears to be a significant process, others being control by organisms and control by a physico-chemical process (the solubility of a hydroxylated magnesium silicate). Clay minerals typical of those suspended

in streams and brought to the sea, release silica and the two systems tend toward similar, intermediate values (Mackenzie et al., 1967).

Control of various ions by clay minerals involves equilibria of the type given (Equation 2) and is discussed elsewhere (Martin, 1970).

CRUSTAL CONCENTRATION

As Goldberg (1965) has noted, the concentration of an element in the marine environment may be low for two reasons: the concentration of the element in the source (crustal rocks or interior of earth) may be low or the element may be abundant in the source but its reactivity limits its concentration in sea water. Lithium is an example of the first condition, and aluminum is an example of the second.

The mean residence time, τ , is often used to correlate the relative reactivities of various elements in the marine environment. For a given element the value of τ is defined as the mean time the element is in sea water before removed by precipitation (Equation 4).

$$\tau = \frac{A}{(dA / dt)} \quad (4)$$

Here, A is defined as the total amount of element suspended or dissolved in sea water, and dA/dt is the amount precipitating or introduced in unit time.

Values of mean residence times (Table 3) seem to fall into three groups. The alkali and alkaline earth metals (except beryllium) have long residence times and low reactivities. (The decrease in residence time with increasing atomic number of the alkali metal ion is consistent with the known parallel increase in retention in clay minerals.) A second group of trace elements have intermediate values and some are elements found in ferromanganese nodules in the oceans (Mero, 1965). The third group is composed of elements that have low residence times because they enter the ocean as solid phases (as clay minerals, volcanic glass, etc.) and because of high reactivities. Elements in the third group have residence times that are less than mixing times and spatial and temporal variations in the concentrations are marked.

TABLE 3
Mean residence times of selected elements*

Category	Element	Mean Residence Time, Years
Long	Sodium	260 million
	Calcium	8 million
	Potassium	11 million
	Lithium	20 million
Medium	Barium	84,000
	Zinc	180,000
	Manganese	1,400
	Cobalt	18,000
Short	Aluminum	150
	Beryllium	100
	Iron	140
	Chromium	350

*From Goldberg (1965)

CONTROL BY PHYSICAL-CHEMICAL PROCESSES

The upper concentration that a metallic ion or an anion might attain in sea water should be governed by the solubility of the least soluble compound. The importance of physical-chemical control by solubility probably has not received the attention it deserved, though excellent treatments of the subject are available (Goldberg, 1965; Krauskopf, 1956; Redfield, 1958, Sillén, 1961). Possibly, the major uncertainties in theoretical and experimental values of solubilities are responsible for the lack of attention. Nevertheless, three examples of the importance of control by solubility can be given here as an indication of the usefulness of the concept. Krauskopf (1956) calculated the theoretical maximum concentrations certain metallic elements would have, based upon the solubilities of compounds that might be formed with major anions of the sea. The results were compared with observed values that were obtained by adding the metal ion, as a solution, to sea water until a precipitate formed. The solids were not characterized, which may be a major fault of the experiment. The agreement between the two values is often close. But it appears that concentrations of many elements (lead, nickel, cobalt, copper, zinc, cadmium, and magnesium) are not controlled by solubility equilibria involving the major anions.

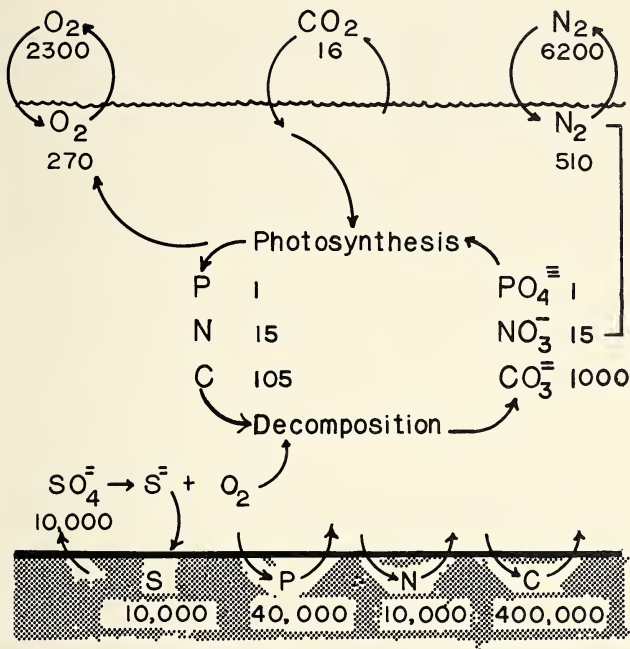


Fig. 1. Relative proportions and interaction of some major elements in the marine ecosystem. Ratios are based on the number atoms per atom of phosphorus in the sea (after Redfield, 1958; Martin, 1970).

The concentrations of calcium, strontium, and maybe barium do seem to be controlled by such equilibria.

The solubility of silica in sea water seems to be controlled to a major extent by the solubility of a hydroxylated magnesium silicate. The solubility of this material seems to limit the dissolved silica in real sea water to about 26 ppm (MacKenzie et al., 1967), though Siever (1962) indicated the concentration in brine or artificial sea water to be much greater (ca. 140 ppm).

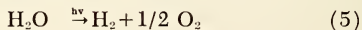
Perhaps the control of phosphate is the most important example of physical-chemical control. Redfield (1958) has suggested that phosphorus is a master element, and this is evident from a consider-

ation of the relative number of atoms of each element in the sea, atmosphere, and earth's crust (Fig. 1). From a standpoint of atomic ratio alone, this seems to be an accurate view, though it does not imply that phosphate concentration limits the growth of these organisms and the question arises of what controls the concentration of the master element, phosphorus. The answer seems to be the solubility of a phosphate compound; which one is uncertain. Available data suggest that the order of solubility is $\text{CaHPO}_4 < \text{Ca}_3(\text{PO}_4)_2 < \text{Ca}_5(\text{PO}_4)_3\text{OH} < \text{Ca}_5(\text{PO}_4)_3\text{F}$. The last two compounds hydroxy and fluoroapatite probably are significant in control of phosphate concentration. Sillén (1961) estimates the phosphate concentration expected from the dissolution of hydroxyapatite is $10^{-7} M$, which compares well with commonly observed values ($10^{-6} - 10^{-8} M$).

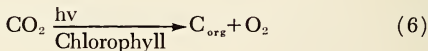
CONTROL BY ORGANISMS

Organisms control the concentrations of many elements in various domains of the sea, but two examples seem particularly appropriate for consideration: control of oxygen in the atmosphere and control of the nitrogen in the sea.

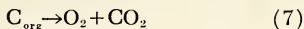
The balance of oxygen in the atmosphere is thought to be controlled by processes occurring in the sea (Redfield, 1958; Martin, 1970). Briefly, we assume the primordial atmosphere was devoid of oxygen and that the molecular oxygen in the present atmosphere is largely the result of a balance of five oxygen-producing and oxygen-consuming processes. These are (1) photochemical decomposition of water (Equation 5)



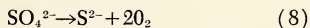
in which photons in the upper atmosphere effect decomposition with hydrogen escaping to outer space, (2) photosynthesis on land and in the sea basically leads to the production of bound organic carbon and oxygen (Equation 6); (3) biochemical oxidation



(Equation 7) is effectively the reversal of the photosynthesis processes, (4) various oxidation processes (oxidation of sulfide and fer-

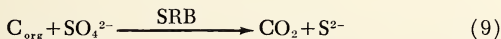


rous minerals, oxidation of volcanic gases, industrial activity) remove oxygen from the atmosphere, (5) the action of sulfate-reducing bacteria (SRB) effectively provides oxygen, according to the overall process (Equation 8)



The relative importance of these processes has varied in geologic history. The first two processes (Equations 5,6) probably were the major oxygen-producing processes in the primitive world. Now, some believe that the major regulatory process is not photosynthesis involving phytoplankton because the combination of Equations 6 and 7 does not lead to a net production of oxygen. Photosynthesis produces a long-term net oxygen increase only to the extent that biological decomposition is avoided, e.g., through burial in an anoxic environment. Such environments are relatively rare on the surface of the earth, particularly in soil.

Redfield (1958) suggested that the action of sulfate-reducing bacteria might be responsible for the maintenance of the oxygen balance in the sea. The net process (Equation 8) actually consists of two steps. The first is production of bound organic carbon at the sea surface (Equation 6). The second involves utilization of dead organisms by sulfate-reducing bacteria (SRB) in an oxygen-poor environment (Eqn. 9)



The existence of suitable environments in or near the world ocean is probably more extensive than generally believed and the importance of sulfate-reducing bacteria probably deserves more attention (Martin, 1970).

Organisms are involved in the nitrogen cycle of the sea in many

significant stages (Martin, 1970). Perhaps their most striking role is in resolving the evident imbalance in the nitrogen budget. We can summarize the consequences as described by Rittenberg (1963) and Sillén (1965) among others.

The second possibility, a missing entry, seems more reasonable, and it has been assumed to be denitrification, the biological reduction of nitrate (or nitrite) ion to nitrous oxide or molecular nitrogen. Denitrifying bacteria are known, for example, and they function in an oxygen-poor or anoxic environment.

The absence of suitable environments is a major difficulty in advancing denitrification as the missing entry in the nitrogen budget. For example, the estimated area and volume of appropriate sediments seems to account for only 10 per cent of the imbalance (Rittenberg, 1963).

Obviously, other localities must be involved. These are anoxic environments, (e.g., in the Black Sea, the Cariaco Trench, and certain Norwegian Fjords), intermittantly stagnant basins (e.g., the Gotland basin in the Central Baltic), and in the oxygen-minimum layers (Martin, 1970). The last possibility includes broad expanses of the tropical Indian and Pacific Oceans. Here, at about 150-800 meters, the dissolved oxygen concentration is very low. Goering (1968) has measured roles of denitrification in this layer by means of a ^{15}N -tracer technique. The layer is a site of active denitrification, but the extent of the process and the responsible organisms deserve more discussion and investigation (Martin, 1970).

SUMMARY

We have provided only partial answers to the questions raised initially. The apparent constancy of the sea is basically due to two causes. First the limitations of our analytical methods have not always allowed us to detect many subtleties that occur, though these limitations are becoming less restrictive. Second, the gross constancy of many properties may be ascribed to a marvelous balance that includes the few processes considered here. Control by weathering, action of clay minerals, crustal concentration, solubility limitations, and organisms is significant; the interrelationship between processes is far more significant.

TABLE 4
Nitrogen budget of the Sea*

Entry	Amount†
Reserve in Ocean	920,000
Annual use by phytoplankton	9,600
Annual contribution by:	
Rivers (dissolved N)	19
Rivers (suspended N)	0
Rain	59
Annual loss to sediments	9

*Rittenberg, 1963

†Units, million meter tons

The nitrogen budget of the sea (Table 4) appears to be unbalanced, i.e., the input from the land and atmosphere does not balance the nitrogen lost to the sediments (In contrast the phosphorus and silicon budgets appear to be balanced). The annual excess input is thought to be about 70 million meter tons (Table 4, Entry 3-4) if the ocean has attained a steady-state condition that we assume. Nitrogen must escape from the sea; otherwise, the annual loss of nitrogen to the sea should deplete atmospheric nitrogen in 400 million years (less than 20 per cent of the estimated age of the earth). Also, at the pH and pE (cf. Martn, 1970) of the ocean, molecular nitrogen should be irreversibly converted to nitrate ion (Sillén, 1965).

Two explanations of the imbalance are available, (1) the data are incorrect, or (2) an entry is missing.

The data in Table 4 have uncertainties, but there is no reason to believe they are erroneous and other estimates using different approaches yield a similar estimate (Martin, 1970).

ACKNOWLEDGMENT

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